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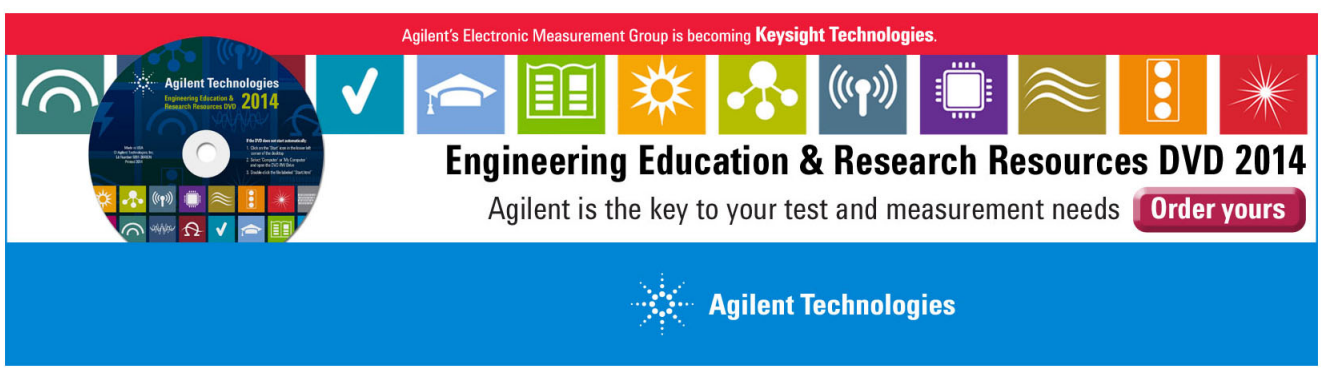

Growth and stability of Pt on Au nanorods

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We present a systematic study of Pt overgrowth on Au nanorods via a wet chemistry approach. The atomic resolved imaging provides direct evidence of initial epitaxial growth of Pt on the surface of Au nanorods, with a preferential deposition occurring at the rod ends. Over a period of one and half years, the carbon-supported nanorods are shown to have undergone a structural transformation when they are kept at ambient conditions, in contrast to the rods kept in solutions whose structure remains stable. Further controlled experiments show morphological changes of the nanorods upon annealing. We discuss the results in terms of the role that kinetics vs. thermodynamics plays in the observed phenomena. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4751288]

Gold nanoparticles have been extensively investigated and can now be made in relatively large quantities with well-defined shapes and uniformities.[1–3] They are often used as a platform for the deposition of an additional metal, which allows the chemical and physical properties of these bimetallic nanomaterials to be further modified by varying composition and chemical ordering.[4–7] The Au-Pt bimetallic systems are particularly interesting for their potential applications as catalysts in the automobile industry, in which a long-term materials stability is essential.[8,9]

It is well known that no solid solution can be formed between bulk Au and Pt.[10] However, at a reduced length scale, the equilibrium structure of Au-Pt is still unclear.[11] Even though Luo *et al*. showed that AuPt alloyed particles (~2 nm) can be prepared using a two-phase synthesis protocol,[12] recent theoretical calculations suggest that a core-shell structure of Pt/Au with Au at the surface is preferred at the size of several hundred atoms.[13] Further, there is overwhelming experimental evidence showing the chemical synthesis of Pt onto Au seed nanoparticles,[14–19] though limited data are available at present in terms of the stability of these bimetallic nanoparticles with inversed chemical order.

In this study, we report our detailed characterization of Pt overcoated Au nanorods, via aberration-corrected scanning transmission electron microscopy (STEM) based techniques. We focus our attention on the growth mode and their long-term stability under controlled external environments.

Gold nanorods (Au NRs) were prepared using the seed mediated growth method reported by Nikoobakht and El-Sayed.[20] The synthesised gold nanorods were centrifuged at 6000 rpm for 20 min and re-dispersed in Milli-Q water twice to remove excess surfactant (cetyl trimethylammonium bromide—CTAB). Prior to Pt deposition, the Au NRs were centrifuged again at 6000 rpm for 20 min and re-dispersed in 0.1 M CTAB solution; the presence of CTAB enables reproducible Pt deposition on the Au NR surface to occur without further aggregation of particles. The Pt deposition was adapted from Grzelczak *et al*.[18] Calculated amounts of the $PtCl_4^{2-}$ solution were mixed with 1 ml of the Au NRs for 30 min at 40 °C in order to achieve Pt:Au molar ratios of 0.05, 0.25, 0.5, and 0.75. This was followed by addition of a known amount of ascorbic acid (AA) to make a final AA:Pt ratio of 10:1 for all compositions. The solutions were kept at 40 °C for 20 h, during which time their color changed from purple to dark grey, indicative of the formation of Pt coverage on the Au NR surface. The resulting solution was centrifuged three times at 6000 rpm for 20 min and re-dispersed in Milli-Q water.

STEM observations were carried out using a JEOL 2100F microscope equipped with a CEOS aberration corrector, operated at acceleration energy of 200 kV. High angle annular dark field (HAADF) images were recorded using a JEOL ADF detector. The microscope is also equipped with a Bruker XFlash 4030 SDD detector, enabling energy dispersive x-ray spectroscopy (EDX) analysis.

Figure 1 shows STEM-HAADF images obtained from the as-grown Au nanorods (a) and Pt on Au nanorods with Pt:Au ratios of 0.05, 0.25, 0.50, and 0.75, in (b)–(e), respectively. A change in surface morphology with the increasing level of Pt coverage was apparent, where the initial growth preference was seen at the tips of the nanorods. Such a preferential growth persisted when the Pt:Au ratio was the highest, being 0.75 in our case, as evidenced by the corresponding nanorods becoming dumbbell-shaped, shown in Fig. 1(e).

The deposition of Pt onto Au nanorods was further confirmed by EDX mapping. Figures 2(a)–2(c) display elemental maps of Au, Pt, and Ag, respectively. Fig. 2(e) is the corresponding STEM-HAADF image taken from the same rod. The overlap of the elemental maps in Fig. 2(d) shows the relative location of Au and Pt, that support the overall core-shell structure, in agreement with the general picture accepted for the sequential chemical deposition of Pt on Au nanorods.[19] The Ag signals are likely to arise from the residue from the synthesis of Au nanorods.

Atomically resolved STEM-HAADF imaging provides direct evidence that the initial Pt deposition follows an epitaxial growth mode on the surface of Au nanorods. Figure 3 is a representative image taken from the sidewall of AuPt nanorods, along the [100] zone axis. Pt and Au have similar atomic numbers (Z = 78 and 79, respectively). Therefore, the

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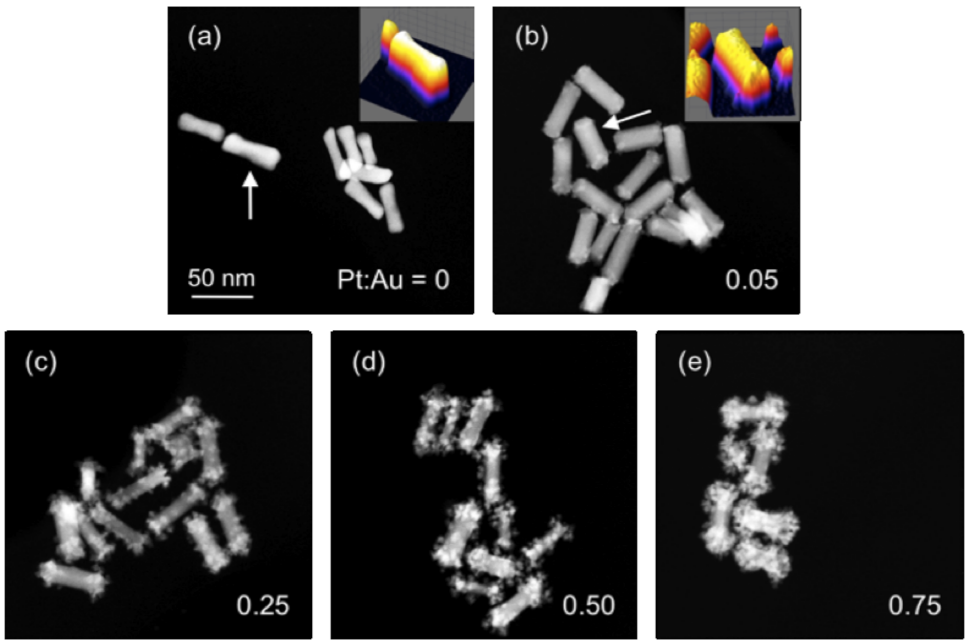

FIG. 1. HAADF-STEM images taken from (a) the as-grown Au nanorods (NR), and Pt-coated Au NRs with Pt:Au ratios of (b) 0.05, (c) 0.25, (d) 0.50, and (e) 0.75. The 3D intensity profiles from an as-grown Au NR (arrowed) and a Pt-coated NR (arrowed) are inset in (a) and (b), respectively.

HAADF intensity difference can be attributed mainly to thickness contrast, rather than Z-contrast.[21,22] This allows us to associate the sharp intensity variation appearing at the Au-Pt boundary to the island formation of Pt. Here, the Pt overlayer has a well-defined cube-on-cube orientation relationship with the underlying Au nanorods. This epitaxial growth is seen in some areas to be extended up to 9 layers of Pt. Considering the difference in lattice parameters of bulk Au and Pt (see Table I), the observed epitaxial growth represents 3.9% lattice strain. The growth mechanism of Pt on crystalline Au(111) and (100) surfaces has been investigated yet remains controversial.[5] It seems that the growth mode is strongly dependent on the conditions of the growth.

The overall AuPt core-shell structure observed in the present study is consistent with the sequence of the deposition. It would be interesting and important to investigate the stability of this structure from both a fundamental and a practical point of view. We found that the AuPt nanorods were stable over a prolonged period up to one and half years, if they were kept in the solution under ambient conditions. However, the morphology evolved over the same period if the nanorods on the standard TEM grids were stored in air

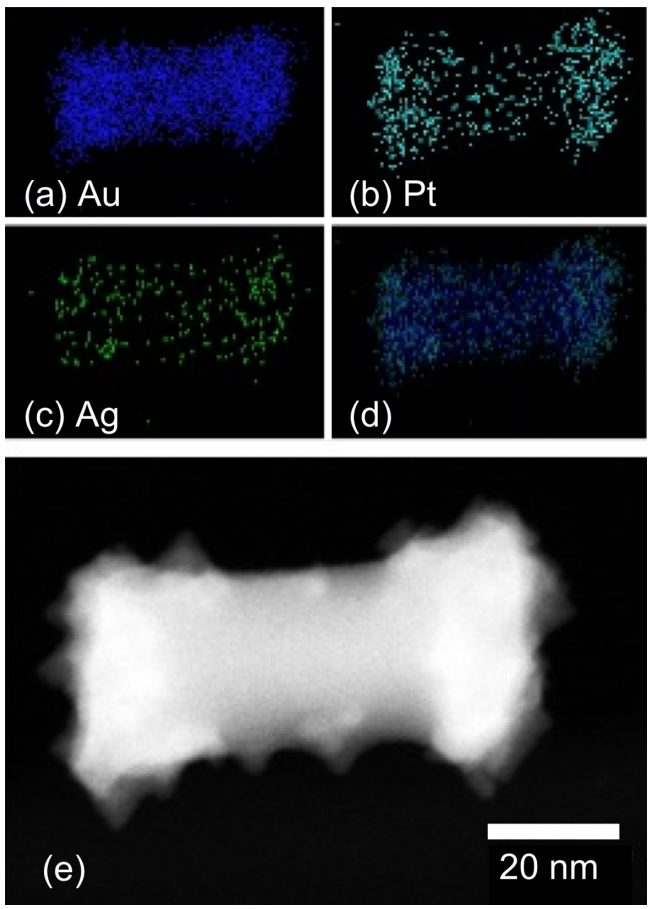

FIG. 2. EDX mapping of a AuPt nanorod with Pt:Au ratio of 0.75: (a) Au signal, (b) Pt signal, (c) Ag signal, and (d) overlapping of Au and Pt signals. The STEM image of the same rod is shown in (e).

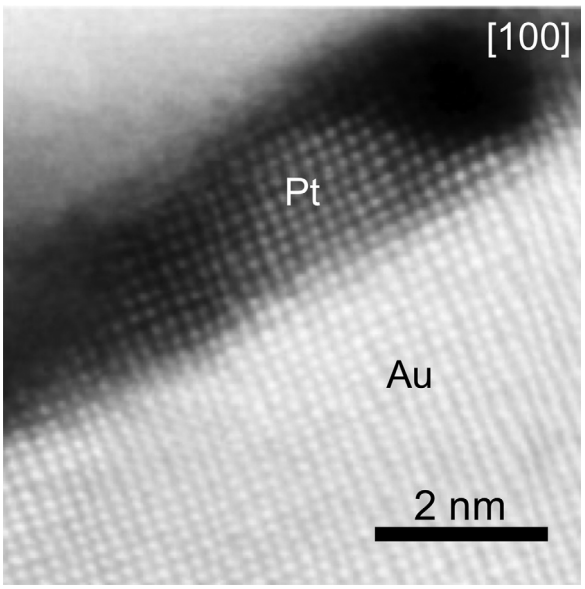

FIG. 3. Atomic resolution HAADF-STEM images showing a Pt particle located on a side surface of a Au nanorod.

TABLE I. Summary of key parameters of Au and Pt for comparison. Data are taken from Refs. 23 and 24.

	Au	Pt
FCC, lattice parameter (Å)	4.08	3.92
Atomic radius (Å)	1.74	1.77
Cohesive energy (eV/atom)	3.81	5.48
Surface energy (J/m^2)	1.50	2.49

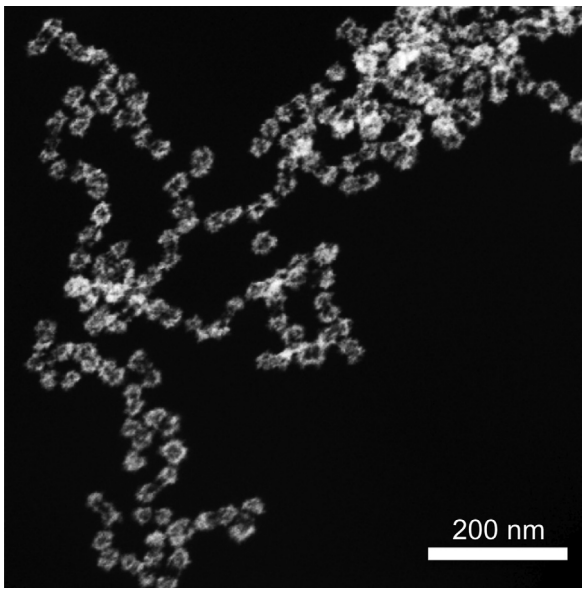

FIG. 4. HAADF-STEM images of AuPt nanorods with Pt:Au ratio of 0.25, after the nanorods were kept on TEM grids in ambient conditions for one and half years.

and at room temperature. This is evident from the image shown in Fig. 4, taken from an aged AuPt sample with a Pt:Au ratio of 0.25 composition. The image should be compared with the one shown in Fig. 1(c), which was taken from the same sample but immediately after its preparation from the solution. It seems that the original Au rod seeds had been dissolved or diffused.

The EDX elemental maps (Fig. 5(a)) of Au and Pt from the aged nanorods confirm that a void within the rod had been formed. It is possible that the original Pt islands may act as the nucleation sites for Au atoms. If this is the case, then the aged nanorods may represent an energetically stable equilibrium state for AuPt bimetallic nanoparticles. It is possible that the presence of surfactant and/or bromide in the solution stabilizes the original Au core-Pt shell structure and that this surfactant is wholly or partially removed under ambient condition.

To further study the driving force of the structural transformation, the AuPt nanorods on a TEM grid were annealed to 200 °C in vacuum of 10^{-6} mbar for 3 h. Similar morphology changes were again observed, though to a slightly lesser extent (see Fig. 5(b)). The result suggests that the initial sequentially deposited Au core Pt shell structure may be due to kinetic trapping. This hypothesis is supported by energetic considerations (Table I): the relatively low cohesive energy and low surface energy of Au in relation to Pt would favor the Au atoms on the surface. We speculate that the diffuse channels for Au atoms onto the Pt islands may be through the initial incomplete Pt coverage on Au seed rods. Blocking these gaps would increase the kinetic barriers for the diffusion of Au, potentially increasing the stability of the bimetallic rods.

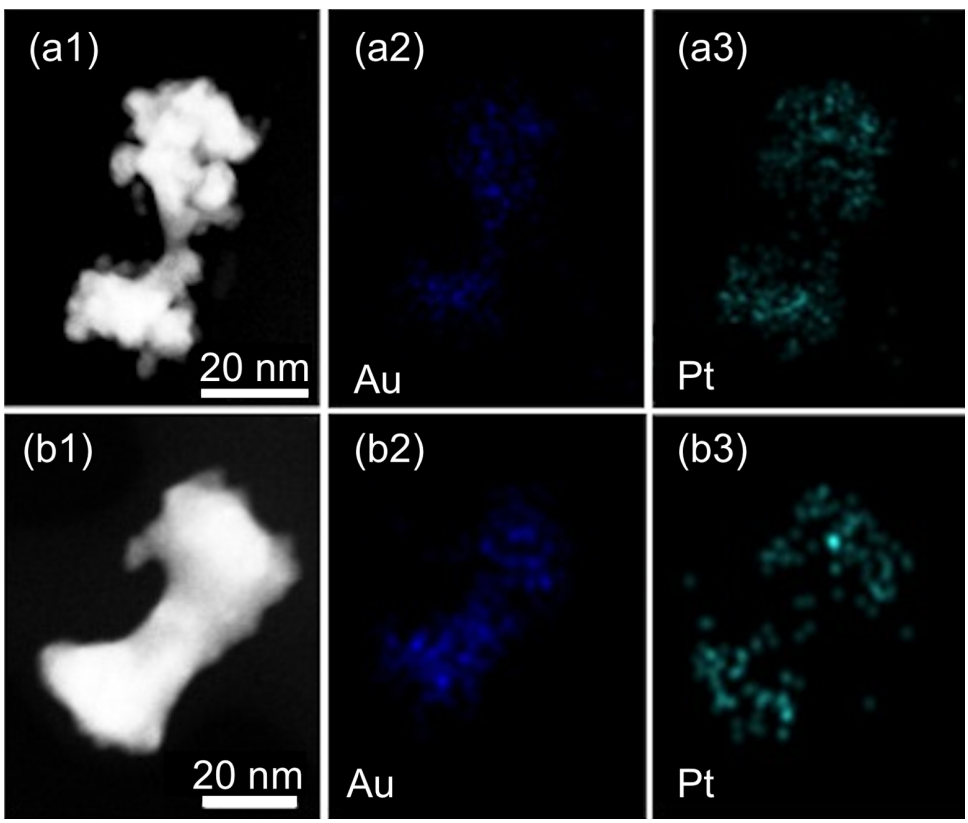

FIG. 5. HAADF-STEM and corresponding EDX images of AuPt nanorods with Pt:Au ratio of 0.25, showing evolution of morphology: after the nanorods were kept on TEM grids in ambient condition for one and half year (a1-3); after the sample was annealed at 200 °C in vacuum for 3 h (b1-3).

In summary, we have shown that Pt deposited on Au nanorods via a wet-chemical route forms an overall core-shell structure, with direct evidence of initial Pt epitaxial growth on Au surfaces, followed by the formation of Pt islands on the Au nanorods. This structure undergoes significant changes when the supported rods are exposed to air or annealed at elevated temperatures, with signs that Au diffuses outwards to form either Pt-Au alloyed or Pt(core)Au(shell) nanoparticles. These findings provide insights of kinetic vs. thermodynamic roles played in structural morphology of Pt on Au seeded nanorods. They may also have implications in potential catalytic applications if Au nanoparticles are to be used as a seed platform for Pt.

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